Research Article

Biomass-Derived Porous Carbon Coated with Silver Nano-ribbon/Polyaniline for Capacitive Deionization

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Abstract

Preparation of a biomass-derived porous carbon containing silver nano-ribbon/polyaniline and its capacitive deionization performance is described in this study. At first porous carbon was derived from a biomass. Then silver nano-ribbon and polyaniline were decorated on the porous carbon via an *in situ* polymerization technique. The porous carbon and its nanocomposite were characterized using scanning electron microscopic techniques coupled with energy dispersive spectrum and FT-IR spectroscopy. The BET analysis revealed that the porous carbon possessed a specific surface area of 369 m^2/g with excellent pore size of 2.2 nm. Further, the capacitive deionization efficiency of the nanocomposite towards groundwater was 79%.

Keywords: Biomass, silver nano-ribbon, polyaniline, capacitive deionization, carbon materials, nanocomposites

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Introduction

The availability of affordable clean water is the major socio-economical as well as technological challenge at present. Indeed, more saline water is available than the fresh water in the world. Conventionally, techniques such as distillation, reverse osmosis, and electrodialysis are implemented for generation of clean water from saline water. In fact, the saline water is a mixture of water (major component) and salts (minor component). Most of the aforementioned conventional techniques generate clean water by separating the major component from the minor component. Consequently the desalination process involves high energy consumption and operational cost in addition to installation costs [1, 2].

Recent trend in desalination is to develop techniques that are more energy efficient and economical [2]. Over the years, capacitive deionization (CDI) is emerging as a suitable technique for desalination of water with low or moderate salt content. This is mainly due to the robustness, energy efficiency and cost effectiveness of the technique. For a better CDI performance, careful selection of materials and design of the electrode are important. One of the strategies is to select a porous material for electrode. Preceding researches indicated that carbon materials such as porous carbon [3], graphene [4], carbon nanotubes, electrospun fibers [5], carbon aerogel [6], and etc [7], were applied for water desalination. It is inevitable that the process of preparation of most of these materials is higher which leads to elevated cost of the clean water. Thus the fundamental question of the "best" material remains unanswered for CDI technique.

Biomass such as wood chips is a renewable, abundant, and economic resource that is conventionally used for energy and production of charcoal. Charcoal has porous structure and widely used as adsorbent, catalyst support, and for separation of gases. In view of developing an efficient and economic electrode material for capacitive deionization, in this study, porous carbon is derived from a biomass and decorated with silver nano-ribbon and polyaniline.

Materials and Methods

Fresh wood chips (500 g) of *Prosopis juliflora* (local name: cheemai karuvel) was collected from Nagapattinam district in Tamil Nadu, India. The wood chips were washed thoroughly with distilled water and kept under shade for a week. The dried wood chips were molded with clay and carbonized in a Muffle furnace at 600 ^oC at air atmosphere for 1 hr with a heating rate of 3^oC/min. On one hand, the carbonized samples were treated with 0.1 M of aniline (Hi-Media) in 1.0 M HNO_3 and reacted with 0.1 M of $AgNO_3$ (Hi-Media) under UV-light (20 W) for 24 h (**Figure 1**). Then the reaction mixture was washed with 1.0 M HNO_3 and distilled water followed by drying under vacuum. On

the other hand, the carbonized samples were grinded manually to obtain homogenous powder and treated similar the precursor described above.

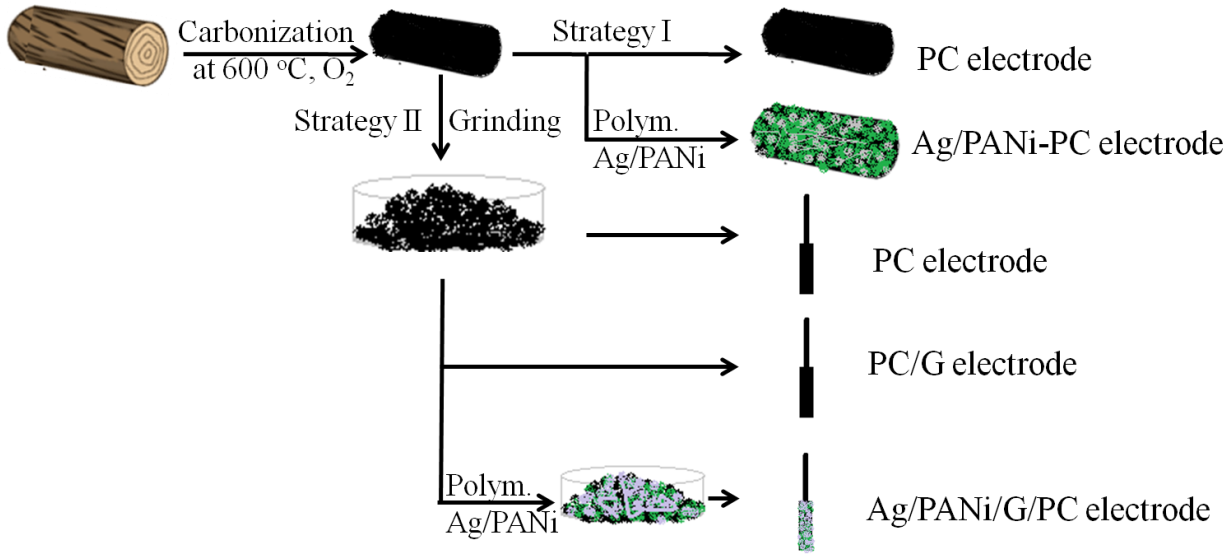

Figure 1 Schematic representation of synthesis of porous carbon-based nanocomposites

The morphologies of porous carbon (PC) or silver nano-ribbon/polyanilne/porous carbon (Ag/PANi/PC) nanocomposite were observed under a scanning electron microscopy (SEM, Hitachi 3000H) coupled with energy dispersive spectrum (EDS) after sputtering the samples with platinum for 120 s. A field-emission scanning electron microscopy (FE-SEM) was also used to observed the morphologies of the samples after sputtering them with osmium for 7s. The Fourier-transform infrared (FT-IR) spectra of the samples were taken using Perkin Elmer- spectrum one instrument. The specific surface area and pore size were evaluated using Brunauer–Emmett–Teller (BET) method (BELSORP-max, BEL Japan, Inc.).

The electrodes for CDI were prepared by mixing 70 wt.% of PC or Ag/PANi/PC nanocomposite with 20 wt.% of graphite, and 10 wt% of adhesive. The mixture was coated homogeneously on aluminium foil of dimension 5 x 3 x 0.3 cm^3. Then the electrodes were dried under vacuum for 24 h. The electrochemical behavior of the samples under cyclic voltammetry technique was carried out using CHI760C instrument at a scan range of -0.2 to 0.8 V and scan rate 0.005 V/s.

The CDI experiment was performed in batch mode. A two electrode cell, consisting of an anode and cathode (5 cm x 3 cm) made up of either PC or Ag/PANi/PC nanocomposite was set up. Both the electrodes were separated by a nylon spacer. The total volume of the cell was maintained at 50 mL. The electrodes were connected to a DC source. The CDI experiment was performed for both NaCl solution (1000 ppm) and ground water.

Results and Discussion

At first the carbonization of the wood chips were carried out similar to conventional technique at laboratory scale. **Figure 2a** and **b** shows the SEM and FE-SEM morphologies of fine porous carbon powder. Apparently, porous carbon prepared under oxygen atmosphere did not exhibit significant conductivity. Therefore, the porous carbon was decorated with silver nano-ribbon/polyaniline (Figure 2c and d) via an in situ polymerization technique. The average diameter of the silver nano-ribbon was 257±36 nm. Further, SEM-EDS of Ag/PANi/PC nanocomposite revealed the presence of Ag and polyaniline (Figure 2e). The FT-IR spectra of PC, graphite, PANi, Ag/PANi/PC nanocomposite are shown in **Figure S1**. The peaks at 1571 and 1480 cm^{-1} for Ag/PANi/PC nanocomposite were corresponding to the C=C stretching in quinonoid and bezenoid structures of PANi [8, 9]. C-N stretching of the benzenoid and quinonoid ring found at 1380 and 1290 cm^{-1}, respectively. The peak at 829 cm^{-1} was attributed to aromatic C-H out-of-plane bending of the 1,4-disubsituted benzne ring [10-12]. The results indicated that decoration of silver nano-ribbon/polyaniline on PC is successful.

Figure 3 shows the nitrogen adsorption and desorption isotherms and pore size distributions of the PC and Ag/PANi/PC. The results indicated that the PC exhibited a BET surface area of PC was 369 m^2/g, pore volume of 0.2031 cm^3/g, and pore size of 2.2 nm. Meanwhile, the surface area of Ag/PANi/PC was decreased to 67.1 m^2/g with a pore size of 4.93 nm. Silver nano-ribbon/polyaniline decorated on PC bound the particles together leading to

decrease in surface area [13]. Indeed, the interconnection by silver nano-ribbon/polyaniline helped to decrease the resistance of the PC.

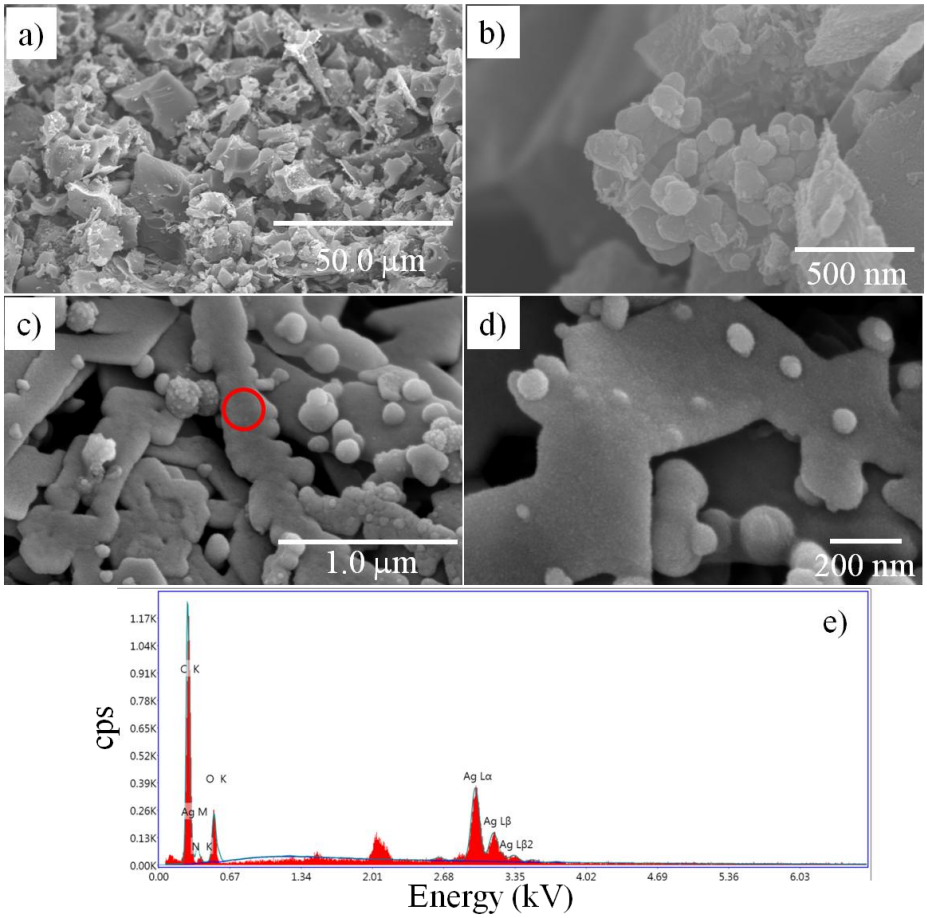

Figure 2 SEM and FE-SEM morphologies of porous carbon (a&b). FE-SEM and EDS of Ag/PANi/porous carbon (c-e)

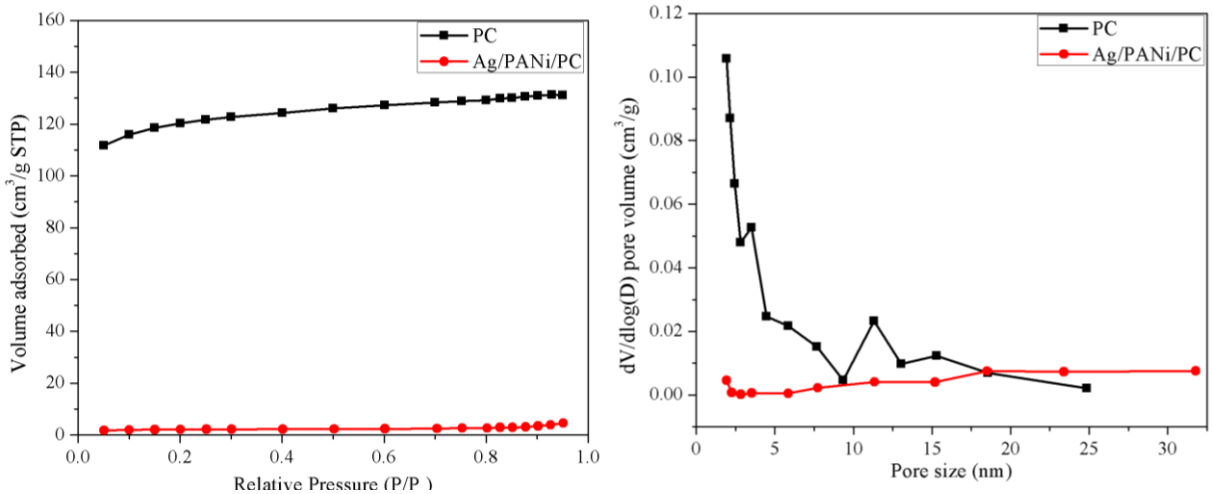

Figure 3 Nitrogen adsorption and desorption isotherms (a) and pore size distributions (b) of the porous carbon (PC) and Ag/PANi/PC

In order to test the deionization potential of the electrodes prepared from both PC and Ag/PANi/PC, the electrodes were evaluated for removal of ions from standard 1.0 M NaCl solution (**Table S1**). At first the voltage required for CDI was optimized using the DC source. The optimum voltage was 1.0 V and any further increase in voltage led to electrolysis of water in presence of NaCl solution. The CDI rates were calculated based on the ratio between the difference in the initial and final concentration of the solution and the initial concentration. The CDI

results indicated that deionization rate for PC and Ag/PANi/PC were 72.8% and 74.2%, respectively. Similarly, CDI performances for the PC and Ag/PANi/PC electrodes were tested against ground water having 0.99 ppt of total dissolved solids and the results are shown in **Table 1**. The results indicated that the CDI rate is higher for Ag/PANi/PC than the PC electrode. While an external potential is applied to the electrodes, the ions move from the water sample to the electrodes. In this study, at about 10 min of CDI operation, the electrodes became saturated with ions. Then electrode regeneration was conducted by reversing the electric potential for about the same time to the CDI operation. It was noted that different kinetics is involved in ion adsorption on the electrodes. As a result, both adsorption and desorption occur simultaneously during regeneration process [14].

Table 1 Capacitive deionization of ground water

Sample	Conductivity (mS)	TDS (ppt)	Salinity (ppt)	CDI rate (%)*
Distilled Water	0.1	0.06	0	-
Tap Water	1.8	0.99	1	-
CDI Water (PC)	0.7	0.32	0	67.7
CDI Water (Ag/PANi/PC)	0.8	0.21	0	78.8

*Calculated based on TDS.

Conclusion

In this study, a porous carbon was prepared from a biomass which had a surface area of 369 m^2/g. In order to improve the conductivity of the porous carbon it was decorated with silver nano-ribbon/polyaniline nanocomposite. The porous carbon and its nanocomposite were evaluated as potential materials for capacitive deionization of water. The capacitive deionization performance of the nanocomposite was higher than the porous carbon. This is attributed to the interconnectivity rendered by the silver nano-ribbon that led to improved conductivity. The nanocomposite exhibited about 79% of deionization rate. Thus, the porous carbon preparation and conductivity improvement techniques described in this study could be used for scale up of the nanocomposite and used for real time water deionization unit.

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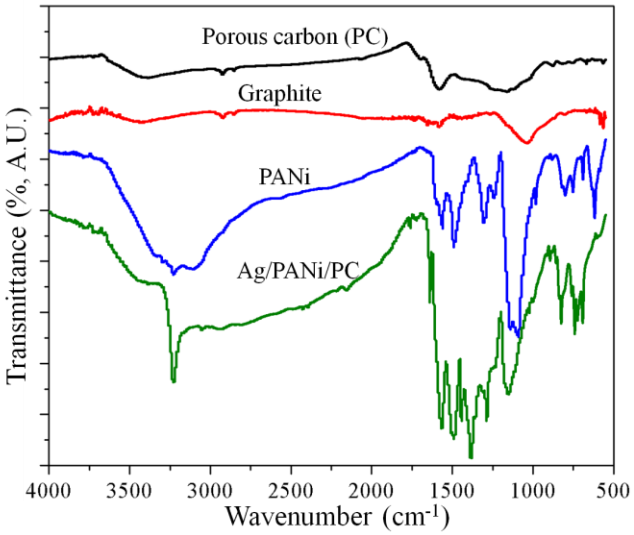

Figure S1 FT-IR spectra of porous carbon, graphite, PANi, and Ag/PANi/porous carbon

Table S1 Analysis of CDI performance using standard sodium chloride solution

Sample	Electrical conductivity (mS)	Sodium (mg/L)	Chloride (mg/L)	CDI rate* (%)
Distilled water	0.1	-	-	-
Std NaCl	2.1	1007	993	-
CDI water (PC)	0.4	276	268	72.8